Response to Comments on WQC for Aluminum and Iron
Related to Busseron Creek TMDL
(November 2008)

IDEM has reviewed the "Technical Comments" dated September 30, 2008 received from Indiana Coal Council (ICC) and their Consultant-ENVIRON International Corp, Denver, Colorado on Busseron Creek TMDL. This IDEM Report pertains to comments on Water Quality Criteria (WQC) for Aluminum and Iron related to Busseron Creek TMDL and offers the Reponses to comments listed below:

Comments: **General and Common to Aluminum and Iron WQC:**

- The TMDL draft claims that the target values shown in Table 5 are aquatic life criteria; they are not. The iron and aluminum values are not even non-rule policy guidance values as they have not been presented to the Indiana WPCB for approval.
- IDEM should have attempted to update these values by updating the toxicity databases and their data validation of all toxicity data, (Refer to Page 5 of ENVIRON Memo).

Response to Comments:

Responses to the above general and common comments are provided below in responses to comments on the respective WQC for Aluminum and Iron.

Comments: **Related to Toxicity Data and WQC for Aluminum:**

- Despite the reference to the IDEM 2005 update, IDEM has not updated their toxicity database for aluminum to recent studies, even in 2005.
- In addition, IDEM did not reference that there was a July 2005 detailed response (from ALCOA to IDEM) requesting further technical clarification of the March 2005 Update; these technical clarifications have yet to be made, (Refer to Page 5 of ENVIRON Memo).
- IDEM has used "the technically flawed 2005 aquatic life chronic concentration, which is presented in the form of dissolved aluminum", (Refer to Page 6 of ENVIRON Memo).

Response to Comments:

IDEM had calculated the site-specific WQC for Aluminum (Al) first in 1996 for the City of Indianapolis followed by in 2002 and then finally updated them in 2005 that are applicable to all warm waters in Indiana outside the Great Lakes System. These site-specific WQC were calculated using toxicity data available in the 1988 Aluminum Criteria Document from 11 Genera of aquatic organisms after removing data for cold water Salmonid species and by adding toxicity data for one more species (*Crangonyx*) to the database. To accomplish the criteria calculations, IDEM had followed the Indiana Rule 327 IAC 2-8.2 and Rule 327 IAC 2-8.3 as well as the 1985 USEPA General Guidance on criteria calculations and the procedure as outlined in the 1988 USEPA Criteria Document on

Aluminum. The recalculation of WQC using toxicity data from 12 Genera obtained from at least 5 or more different families of aquatic organisms as required by the Indiana Rule had resulted in an Acute criterion of 987 ug/L and a Chronic criterion (CAC) of 987 ug/L. The calculated Chronic criterion was then lowered to 174 ug/L to protect some aquatic organisms that dwell in Indiana warm waters. A few other points that provides as a basis in support of the WQC for Aluminum developed by IDEM are as follows:

1. During the course of criteria development for Aluminum and its update in 2005, IDEM had consulted with the USEPA and incorporated various EPA's recommendations about acceptability or non-acceptability of various toxicity data suggested by ALCOA into the criteria calculations for Aluminum. Having done all of the above, IDEM strongly feels that the calculated WQC for Aluminum are valid that could be used with confidence for water quality assessment in warm waters outside the Great Lakes System. It must be pointed out; the IDEM derived Chronic criterion for Aluminum is **174 ug/L** which is at least **2x** higher than the **87 ug/L** Chronic criterion derived by USEPA. Also, lowering of the calculated Chronic value from 987 ug/L to 174 ug/L for Aluminum by IDEM is in concurrence to the 1994 USEPA's Recalculation Procedure Guidance on water quality criteria (see EPA-823-B-94-001) which states that, "The calculated FAV (Final Acute Value), CMC (Criterion Maximum Concentration) and/or CCC (Criterion Continuous Concentration) must be lowered, if necessary, to (1) to protect an aquatic plant, invertebrate, amphibian or fish species that is a critical species at the site ---." A historic perspective and a detailed discussion on development of WQC for Aluminum by IDEM including Comments to the Aluminum criteria calculated by ALCOA was provided in the "**Site-Specific Water Quality Criteria (WQC) for Aluminum: 2005-An Update**", **dated March 2005**. This IDEM document is already referenced in the "Technical Comments" received from Indiana Coal Council (ICC) and should have sufficed and answered all the concerns that are being raised and repeated by the ICC and their Consultant in comments to the Busseron Creek TMDL.

2. However, to answer the so called new comments from ICC and their Consultant (ENVIRON International Corp) about no response from IDEM to comments on site-specific WQC for Aluminum from ALCOA dated July 6, 2005 received through their Legal Counsel-BARNES & THORNBURG, IDEM would like to state that IDEM had provided to ALCOA in depth responses comment-by-comment through IDEM Legal Counsel, Matt Gernand on July 25, 2005. A copy of this IDEM Response document to comments received from ALCOA dated July 6, 2005 is enclosed herewith for immediate reference. This IDEM Response document had several references to the previous March 2005-Update from IDEM, and since both of these documents go together hand in hand; a copy of the IDEM March 2005-Update is also enclosed for a ready reference. A copy of the original July 6, 2005 comments document from ALCOA submitted through their Legal Counsel-

BARNES & THORNBURG is also enclosed to tally each ALOCA comment with the responses provided by IDEM in the IDEM Response document of July 25, 2005

3. IDEM realizes that there may be some more toxicity data out there on Aluminum after 2005. But it must be pointed out here, as was the case in the past with ALCOA, not all published or unpublished articles would be acceptable for criteria calculations. For example in the ALCOA submittal of WQC for Aluminum, except for *Crangonyx* species from 1986 publication, toxicity data for *Daphnia* and *Tubifex* species from 1989 and 1991 publications respectively were not acceptable for criteria calculations for Aluminum. After having several consultations with the USEPA, the exact reasons for not using the new toxicity data from these two species and also not accepting several other changes and modifications made to the existing toxicity data on Aluminum for criteria calculations by ALCOA were provided in the IDEM Update of March 2005, and the same were eluted once more in the IDEM Response to comments document of July 25, 2005.

4. As stated by IDEM in the earlier correspondence to ALCOA, the USEPA is also aware of the various issues related to Aluminum WQC and is working towards solving them. IDEM will revise the Aluminum criteria after USEPA has completed its work on Aluminum criteria issues, but until then the site-specific WQC for Aluminum updated by IDEM in 2005 would be applicable and used in water quality assessment of warm waters in Indiana outside the Great Lakes System.

   Additionally, IDEM had developed the WQC for Aluminum under Article 2 and its applicable two rules cited above well before the Indiana fast track rule become effective in October 2005. Therefore, these or any other site-specific WQC developed earlier to October 2005 do not have to go through the approval process by the WPCB (Water Pollution Control Board) or the USEPA.

   Furthermore, it is highly likely that, even if IDEM were to update the toxicity data on Aluminum in the future and calculate a new set of WQC for Aluminum, the criteria numbers, especially the Chronic criterion of 174 ug/L, is not expected to change very much. The reason being, similar to USEPA, IDEM would have to still lower the newly calculated Chronic criterion value for Aluminum to **174 ug/L** to protect the surrogate of Stripped bass such as Largemouth bass (*Micropterus* sps.), Goldfish (*Carassius* sps.) and Narrow-mouth toad (*Gastrophryne* sps) that occur widely distributed in Indiana warm waters and at a pH range of 7.2 to 8 have 7 - 8 days lower EC_{50} values of **170 mg/L, 150 ug/L** and **50 ug/L**, respectively.

   For IDEM responses to comments on dissolved Aluminum, see the section on "Related to Toxicity Data and Dissolved Versus Total Metal Criteria".

Comments: **<u>Related to Toxicity Data and WQC for Iron</u>:**

- The IDEM memorandum issued in 1997 was not based on a complete list of studies on the aquatic toxicity of iron, in addition the studies that were presented did not undergo data validation and assessment of acceptability, and finally IDEM mixed the toxicity data results for iron (+2), ferrous and iron (+3) ferric in developing a database for iron. It is commonly accepted that species of iron most toxic to aquatic life is ferrous iron, not ferric, (Refer to Page 7 of ENVIRON Memo).

Response to Comments:

As compared to Aluminum, the situation with Iron is entirely different. Unlike with Aluminum, no full fledged criteria document is available from USEPA. Instead, the only document that EPA had put out on Iron is the one in the 1976 Red Book. In this document, based on the limited toxicity information available, EPA had identified <u>1 mg/L</u> as the Chronic criterion for Iron but provided no acute criterion for Iron. This being the case and IDEM as well as many NPDES Permittees needing WQC for Iron for water quality assessments and for effluent discharges to warm waters in Indiana outside the Great Lakes System, in 1997 IDEM had calculated the WQC for Iron. To accomplish this, IDEM obtained majority of toxicity data on Iron from USEPA AQUIRE Database and some data from published literature. Once again, to calculate the WQC for Iron, IDEM had followed the Indiana Rule 327 IAC 2-8.2, **Section (1)** and Rule 327 IAC 2-8.3 as well as the USEPA General Guidance on criteria calculations. The WQC for Iron calculated from toxicity data of <u>10 Genera</u> collected from 5 or more different families of aquatic organism as required by the Indiana Rule had resulted in an <u>Acute criterion of 2,744 ug/L</u> and a <u>Chronic criterion of 2,495 ug/L</u>.

1. In light of the above reasons and discussion, IDEM feels comfortable with the WQC calculated for Iron and stands behind it. Moreover, the IDEM derived Chronic criterion for Iron is **2,495 ug/L** which is almost **2.5x** higher than the **1000 ug/L** (**1 mg/L)** Chronic criterion for Iron proposed by USEPA in the 1976 Red Book. Contrary to this, if IDEM was to follow the guidance in Indiana Rule 327 IAC 2-8.2, **Section (2)**, and use the lowest Species Mean Acute Value (SMAV) of 7300 ug/L available then for the *Daphnia* species, the Chronic criterion for Iron would have been in and around **166 ug/L** or **664 ug/L** as compared to the **1 mg/L** (**1000 ug/L**) Chronic criterion from USEPA.

2. Both USEPA and IDEM are equally aware of the various issues related to WQC for Iron. IDEM will revise the Iron criteria as more toxicity data on various species of Iron become available, but until then the WQC for Iron developed by IDEM in 1997 using Indiana Rule 327 IAC 2-1-8.2 and 327 IAC 2-1-8.3 would be applicable and used in water quality assessments of warm waters in Indiana outside the Great Lakes System.

   For IDEM responses to comments on ferrous (+2) and ferric (+3) iron, see the next section on "--Toxicity Data and Dissolved Versus Total Metal Criteria".

Comments: **<u>Related to Toxicity Data and Dissolved Versus Total Metal Criteria</u>:**

- Clarify if the aquatic toxicity data bases address total or dissolved aluminum, the relationship to pH, iron (+2) or iron (+3), Refer to Page 8 of ENVIRON Memo.
- It is important to note that in regards to metals associated with biological impairment it is the dissolved form of the metal that is commonly accepted as the bio-available form that impacts biological organisms.
- Total concentrations often include particulate and unavailable bound forms of the metal that typically have minimal impact on chemical toxicity to fish and other organisms, (Refer to Page 1 of ENVIRON Memo).

Response to Comments:

In response to the above and some other comments identified earlier, IDEM offers the following responses:

1. As described above, from reasonable to very limited toxicity data were available on Aluminum and Iron, respectively. Consequently IDEM had to use the maximum amount of data that was good and available to calculate the WQC for Aluminum and Iron in 2005 and 1997, respectively.

2. Both USEPA and IDEM recognizes that dissolved forms of metal are more toxic than total and in most natural aqueous systems most metals bind to suspended solids in waters and renders them as less bioavailable or less toxic. Here, it must be pointed, as compared to the bound forms; both Aluminum and Iron also exist as hydroxides in waters and are regarded as dangerous forms that may be harmful as well as toxic to many aquatic organisms.

   Additionally, dilute Aluminum solutions are known to form particles and large insoluble polynuclear complexes known as flocs as a function of organic acids and hydroxide ions in surface waters. Even laboratory studies conducted in alkaline pHs have reported formation of flocs in the exposure chambers. These flocs of Aluminum tend to settle down and have been reported to blanket a stream bed. It is possible that such Aluminum flocs might even impact the many bottom-dwelling organisms, see the 1988 Aluminum Criteria Document.

3. Furthermore, Aluminum is known to be toxic at low pH and at pH <7.0 or at acidic pH, even bound form of Aluminum may become dissolved in acidic environment such as associated with the gills and gut of aquatic organism rendering the same metal as more soluble and toxic to aquatic organisms than otherwise expected. <u>Therefore, it is incorrect to say that only the soluble but not the bound or insoluble Aluminum in water is not likely to cause toxicity and harm to aquatic life</u>.

4. With regard to Iron, IDEM recognizes that similar to Aluminum, Iron exists in many chemical forms in water such as chlorides, hydroxides etc. Besides,

there are always some Iron species that exists both in soluble or Ferrous (Fe^{+2}) and insoluble or Ferric (F^{+3}) form in the water. It is well known that as compared to the Ferric (F^{+3}) Iron, it is the soluble form of Iron (Fe^{+2}) that is more toxic to aquatic life.

Also, similar to Aluminum, Iron remains dissolved as long as the water is acidic and become toxic to aquatic organisms. This is also likely to happen in the acid environment associated with the gill and gut of aquatic organisms. Even otherwise, at alkaline pH (i.e. at pH > 7.0 and above) or due to aeration in ambient waters, most of the dissolved Iron species are hydrolyzed and subsequently oxidized to insoluble Iron compounds. The Insoluble iron in turn may precipitates out and settles down at the bottom of streams and river beds creating smothering effects that could be particularly detrimental to fish eggs and bottom-dwelling fish food organisms. <u>It is also well known that even the insoluble Iron present as hydroxides in water at low to high concentrations may cause respiratory distress and results in damaged gills and in increased susceptibility to diseases and thus be harmful to aquatic life</u>.

5. Finally, both USEPA and IDEM realizes that for calculation of WQQ not only for Aluminum and Iron but even for many other metals, it would be ideal to have WQC calculated for soluble metals. But because of the various chemical and physical conditions discussed above, (e.g., water pH and aeration etc.) it is difficult to conduct aquatic toxicity tests where metals are always present in the soluble form during the entire test period. For example, such as with Aluminum at an alkaline pH in the test solution or with Iron at alkaline pH and aeration in the test chamber, this may render some of the soluble form of Aluminum or Iron metal into an insoluble form. Of course one can measure both soluble and insoluble forms of metal in the test solutions, but majority of the toxicity data currently available for either Aluminum or Iron is devoid of such clear cut information. Consequently, IDEM had to depend on the toxicity data for Aluminum available in the National Database (Aluminum Criteria Document) and some other sources referenced in the IDEM March 2005-Update, and for both species of Iron (Fe^{+2} and F^{+3}) or total Iron on toxicity data mostly retrieved from the USEPA AQUIRE Database and some from published literature. A statement to this effect on data sources for both Aluminum and Iron was already included in the IDEM March 2005-Update and in the 1997 IDEM memorandum that are referenced in the "Technical Comments" received from ICC to Busseron Creek TMDL. Furthermore, as recommended by USEPA, IDEM had to treat this entire toxicity data equivalent to acid-soluble fraction to calculate the WQC for Aluminum and Iron and implement them for water quality assessments appropriately as dissolved or total recoverable metal. An alternative to this approach, Conversion Factors to convert from Total to Dissolved metal or vice-versa would have been ideal, but unfortunately unlike for many other metals no such Conversion Factors for either Aluminum or Iron are available from USEPA at this time.